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TRANSLATION

German Unexamined Patent Application DE 41 25 477 A 1  
("Offenlegungsschrift")

Title: Polyvinylhalogenidharzmasse mit verbessertem Verarbeitungsverhalten

Internat. Class.: C 08 L 27/02, C 08 L 51/02, // C08L 27/02, C08F 283/02, 2/22

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**Polyvinyl Halide Composition with Improved Processing Characteristics**

Polyvinyl halide composition containing 0.1 to 20 wt %, based on the amount of polyvinyl halide, of a two-stage emulsion polymer consisting of

50 to 80 wt % of a first stage made from

80 to 99.5 wt % of methyl methacrylate  
0.5 to 9.9 wt % of a C<sub>1</sub>-C<sub>12</sub> alkyl acrylate and  
0 to 10.1 wt % of other comonomers, and

20 to 50 wt % of a second stage made from

70 to 90 wt % of methyl methacrylate  
10 to 30 wt % of a C<sub>1</sub>-C<sub>12</sub> alkyl acrylate and  
0 to 20 wt % of other comonomers.

## DESCRIPTION

The invention relates to polyvinyl halide compositions containing 0.1 to 20 wt %, based on the amount of polyvinyl halide, of a two-stage emulsion polymer consisting of

50 to 80 wt % of a first stage made from

80 to 99.5 wt % of methyl methacrylate  
0.5 to 9.9 wt % of a C<sub>1</sub>-C<sub>12</sub> alkyl acrylate and  
0 to 10.1 wt % of other comonomers, and

20 to 50 wt % of a second stage made from

70 to 90 wt % of methyl methacrylate  
10 to 30 wt % of a C<sub>1</sub>-C<sub>12</sub> alkyl acrylate and  
0 to 20 wt % of other comonomers.

The invention also relates to the use of the two-stage emulsion polymer as processing aid in polyvinyl halide compositions.

In the processing of polyvinyl halide compositions, particularly of polyvinyl chloride compositions, to shaped articles, short gel and plasticization times of the polymer composition are particularly desirable, because the processing temperatures are close to the decomposition temperature of the polyvinyl halide.

Processing aids, for example copolymers of methyl methacrylate and an alkyl acrylate, can be added to polyvinyl chloride compositions to shorten their gel and plasticization times (DE-A-21 26 924 and DE-A-21 01 808).

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DE-A-22 13 214 discloses graft copolymers consisting of 50 to 99 wt % of a graft core derived primarily from methyl methacrylate and 1 to 50 wt % of a graft shell derived from methyl methacrylate and 10 to 45 wt % of an acrylate ester.

The hitherto known processing aids, however, are not entirely satisfactory in terms of gel and plasticization times.

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The object of the present invention is to eliminate this drawback.

In pursuing this objective, the polyvinyl halide compositions defined hereinabove were found:

The polyvinyl halide compositions preferably contain 1 to 10 wt %, particularly 1 to 7 wt % of the two-stage emulsion polymer, based on the amount of polyvinyl halide.

The amount of the C<sub>1</sub>-C<sub>18</sub> alkyl acrylate used in the second stage is preferably at least 5 wt % higher, and particularly at least 10 wt % higher, than in the first stage.

The emulsion polymer preferably consists of

60 to 80 wt % of the 1st stage and  
20 to 40 wt % of the 2nd stage.

The 1st stage is preferably derived from

90.1 to 95 wt % of methyl methacrylate and  
5 to 9.9 wt % of a C<sub>1</sub>-C<sub>18</sub> alkyl acrylate.

The 2nd stage is preferably derived from

70 to 80 wt % of methyl methacrylate and  
20 to 30 wt % of a C<sub>1</sub>-C<sub>18</sub> alkyl acrylate.

Preferred C<sub>1</sub>-C<sub>18</sub> alkyl acrylates are methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate.

C<sub>1</sub>-C<sub>6</sub>, and particularly C<sub>1</sub>-C<sub>4</sub>, alkyl acrylates are preferred for the 1st stage, and C<sub>6</sub>-C<sub>18</sub>, and particularly C<sub>6</sub>-C<sub>12</sub>, alkyl alkylates are preferred for the 2nd stage.

Preferred other monomers are styrene,  $\alpha$ -methylstyrene, acrylonitrile, methacrylonitrile, vinyl esters such as vinyl acetate and vinyl propionate, and C<sub>7</sub>-C<sub>18</sub> alkyl methacrylates.

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The two-stage polymer is prepared by emulsion polymerization in a known manner.

Suitable emulsifiers are, for example, the alkali metal salts of long-chain fatty acids, alkyl sulfates, alkyl sulfonates, alkylated arylsulfonates and alkylated biphenyl ether sulfonates, salts of abietic acid or of derivatives thereof and of sulfosuccinate esters.

Suitable initiators are, for example, sodium, potassium and ammonium persulfate, tert-butyl hydroperoxide, water-soluble azo compounds such as the salts of 4,4'-azobis(4-cyanoanisic acid) or 2,2'-azobis(2-aminopropene hydrochloride). For polymerizations at relatively low temperatures, redox systems of a persulfate or a hydroperoxide in combination with a reducing agent and an iron(II) salt are particularly well suited. Suitable reducing agents are, for example, sodium metabisulfite, sodium hydroxymethanesulfinate and ascorbic acid.

The emulsion polymerization is preferably carried out at a temperature between 30 and 95 °C.

The polymerization temperature has an effect on the molecular weight of the polymer formed, namely the higher the temperature the lower is the molecular weight. The polymerization temperature for the two stages of the polymer can be equal or different. Molecular size, as a rule, is characterized with the aid of a viscosity measurement. A useful quantity in this respect is the K value<sup>1</sup> of Filgentzcher. The K value of the said polymers, as measured on a 1% solution in tetrahydrofuran, is from 80 to 150, preferably from 90 to 130 and particularly from 100 to 120.

The monomers of the first stage are polymerized first. The monomers of the first stage are preferably polymerized to an extent of more than 95 wt %, particularly more than 99 wt %, before the addition of the monomers of the second stage is started.

The particle size of the emulsion polymers can be adjusted by appropriate selection of polymerization conditions as described, for example, in DE-C 22 30 989. The particle size depends, for example, on the agitator speed. An average (volume average) particle diameter  $d_{50}$  of about 50 to 300 nm is preferred.

<sup>1</sup> The K value is a measure of the degree of polymerization; used in Germany — Translator

The solids content of the emulsions is preferably 30 to 60 wt %. The polymer can be isolated from the emulsion as a virtually water-free powder by precipitation and subsequent drying or, in a single processing step, by spray drying.

Spray drying can be carried out in the known manner as described, for example, in the "Spray Drying Handbook" (K. Mosters, New York, 1985). The drying gas temperature at the inlet to the spray drying tower is advantageously from 100 to 200 °C, and the temperature of the dried powder at the outlet from the spray drying tower is preferably from 40 to 100 °C.

The average particle diameter of the resulting free-flowing powder is, in general, from 50 to 500 µm, particularly from 100 to 300 µm.

Powders that are readily processable and free-flowing and do not tend to "cake" are obtained when the softening temperature (Vicat B as determined by German Standard DIN 53 460) is above 80 °C. Advantageously, therefore, the total amount of C<sub>1</sub>-C<sub>18</sub> alkyl acrylate in the two-stage emulsion polymer should not exceed 15 wt %. A higher amount of C<sub>1</sub>-C<sub>18</sub> alkyl acrylate causes the softening temperature to drop to an undesirably low level.

The polyvinyl halide in the polyvinyl halide composition according to the invention can be, in particular, a homopolymer of vinyl chloride, a copolymer of vinyl chloride with at least 80 wt % of vinyl chloride units in the molecule or a post-chlorinated polyvinyl chloride. The homopolymers of vinyl chloride (polyvinyl chloride) are preferred.

Besides the emulsion polymer and the polyvinyl halide, the polyvinyl halide compositions according to the invention can contain other additives, for example modifying agents for improving impact resistance, heat deflection temperature and weathering resistance, furthermore stabilizers, lubricants, fillers, dyes and pigments. In general, the total amount of other additives is below 40 wt %, particularly below 30 wt %, based on the amount of polyvinyl halide.

The polyvinyl halide compositions according to the invention can be prepared by mixing the powdered two-stage emulsion polymer with a polyvinyl halide and optionally other additives by a conventional method, for example in an extruder, kneader or roll mill.

The polyvinyl halide composition can be converted into the desired shape by methods

commonly used for thermoplastics (extrusion, injection molding, calendering, compression molding, drawing etc).

The polyvinyl halide compositions according to the invention are characterized by short gel and plasticization times. Such short gel and plasticization times result in faster and thus more economical processing.

### EXAMPLE

#### Preparation of the Two-Stage Emulsion Polymer

##### **Graft Copolymer A**

This copolymer was prepared by using the following starting mixtures.

##### Reactor charge:

10 rpm	2200 g	of water
	0.032 g	of iron(II) sulfate heptahydrate
	6.4 g	of tetrasodium pyrophosphate
	3.2 g	of lauric acid
	2.56 g	of 25% sodium hydroxide solution
	3.2 g	of sodium persulfate

##### Feed Mixture 1

2430 g	of water
32 g	of lauric acid
25.6 g	of 25% sodium hydroxide solution
1560 g	of methyl methacrylate
40 g	of methyl acrylate

##### Feed Mixture 2

500 g	of water
3.2 g	of sodium metabisulfite
3.2 g	of 25% sodium hydroxide solution

##### Feed Mixture 3

50 g	of water
3.2 g	of sodium persulfate

Feed Mixture 4

1280 g. of methyl methacrylate  
320 g. of butyl acrylate

272 g. of feed mixture 1 was added to the reactor contents, and the mixture was heated to 60 °C with agitation. At this temperature, the remainder of feed mixture 1 and 40% of feed mixture 2 were added at a uniform rate over a period of 2 h, after which the mixture was allowed to agitate for an additional hour at 60 °C. Feed mixture 3 was then added all at once and feed mixture 4 was added over a period of 2 hrs. The remaining 60% of feed mixture 2 was added over a period of 2 h starting at the same time as the addition of feed mixture 4. The resulting dispersion had a solids content of 37.6 wt % and pH 9.1.

Emulsion polymers B through G and reference polymers a and b were prepared in the same manner.

Table 1 shows the composition of the emulsion polymers. The softening temperatures (Vicat B, DIN 53 460) and the total alkyl acrylate content of the two-stage emulsion polymer are listed in Table 2.

**Table 1**  
Composition of the Emulsion Polymers

Graft Copolymer	1st Stage, wt %	Composition, wt %				2nd Stage, wt %	Composition, wt %			
		MMA	MA	BA	EHA		MMA	BA	EHA	EA
<i>According to invention</i>										
A	50	97.5	2.5			50	80	20		
B	50	92.5	7.5			50	80	20		
C	50	99	1			50	80	20		
D	55	97			3	45	80	20		
E	60	95			5	40	75		25	
F	75	92	8			25	85		15	
G	70	95			5	30	72		28	
<i>Reference</i>										
a	10	100				90	78		22	
b	80	100				20	35		65	

**Expansion of the abbreviations:**

MMA: methyl methacrylate  
MA: methyl acrylate  
BA: butyl acrylate

EHA: ethylhexyl acrylate  
EA: ethyl acrylate

Table 2

Example	A	B	C	D	E	F	G	a	b
Melt, °C	86	84	87	85	82	98	88	68	98
Acrylate content, %	11.3	13.8	10.5	10.7	13	9.8	11.9	19.8	13

Evaluation of the Processing Characteristics of Polyvinyl Chloride Compositions

A base mixture of the following was first prepared in a heated mixer at 120 °C.

100 wt %	of polyvinyl chloride made by suspension polymerization (K value 68)
1 wt %	of tribasic lead sulfate
0.3 wt %	of lead stearate
0.6 wt %	of C <sub>16</sub> /C <sub>18</sub> fatty alcohol and
0.1 wt %	of calcium stearate.

Processing characteristics were then determined in a Brabender Plasticorder (model W 30 H) with a kneading chamber volume of 30 cm<sup>3</sup>. For each test, 31 g of mixture was used. Said mixture consisted of 0.6 g of emulsion polymer in 30.4 g of base mixture in the case when 2% of the emulsion polymer was added, and of 1.5 g of emulsion polymer in 29.5 g of base mixture when 5 wt % of the emulsion polymer was added.

Processing characteristics were determined at 170 °C at a rotation speed of the clockwise-rotating blade of 40 rpm. The ratio of the rotation speed of the counterclockwise-rotating to that of the clockwise-rotating blade was 1.5:1.

The change in torque during the test was recorded by means of a recorder, and from the resulting curve the gel time and plasticization time, defined as the maximum and the minimum of said curve, were determined (see Table 3).

Table 3

Gel and Plasticization Times of Polyvinyl Chloride Compositions

Emulsion Polymer	Amount Added, wt %	Gel and Plasticization Times	
		Gel Time, s	Plasticization Time, s
-	-	51	870
A	2	36	114
	5	18	60
B	2	24	108
	5	24	72
C	2	48	138
	5	24	72
D	2	51	147
	5	24	57
E	2	59	168
	5	24	60
F	2	54	180
	5	30	99
G	2	51	186
	5	27	102
?	2	63	174
	5	30	102
b.	2	72	216
	5	30	108

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**PATENT CLAIMS**

1. Polyvinyl halide compositions containing 0.1 to 20 wt %, based on the amount of polyvinyl halide, of a two-stage emulsion polymer consisting of

50 to 80 wt % of a first stage made from

80 to 99.5 wt % of methyl methacrylate  
0.5 to 9.9 wt % of a C<sub>1</sub>-C<sub>18</sub> alkyl acrylate and  
0 to 10.1 wt % of other comonomers, and

20 to 50 wt % of a second stage made from

70 to 90 wt % of methyl methacrylate  
10 to 30 wt % of a C<sub>1</sub>-C<sub>18</sub> alkyl acrylate and  
0 to 20 wt % of other comonomers.

2. Use of the emulsion polymer according to Claim 1 as processing aid in polyvinyl halide compositions.

3. Shaped articles made of polyvinyl halide compositions according to Claim 1.

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